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KINETICS OF THE GELATION OF COLLOIDAL SILICA AT GEOTHERMAL CONDITIONS, AND IMPLICATIONS FOR RESERVOIR MODIFICATION AND MANAGEMENT

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ABSTRACT

Gel deployments to divert, direct and control fluid flow have been extensively and successfully used in the oil and gas industries for enhanced oil recovery, and for the containment of radioactive and toxic wastes. However, to the best of our knowledge, gels have not been applied to hydrothermal systems to enhance heat extraction. The ability to divert and control fluid flow in the subsurface would be extremely useful to the geothermal industry. Gels may be able to block hydraulic short circuits, minimize losses of injected geothermal fluid to the surrounding formation, and divert working fluids to the hotter regions of a formation. These applications will all in turn maximize heat extraction from a geothermal reservoir and therefore maximize the longevity and the economic potential of the reservoir. Inorganic, non-toxic gels, such as colloidal silica gels, may be ideal blocking agents for geothermal systems if suitable gelation times and control of gelation behavior can be achieved. In the current study, we detail colloidal silica gelation times, behavior, and gel stability as a function of silica concentration, pH, salt concentration, and temperature up to 300 °C. Results indicate that while colloidal silica gels will have limited use in high-temperature geothermal systems ($T > 200$ °C) due to fast gelation times and lack of long-term thermal stability of silica gels at such high temperatures, colloidal silica gels are generally well-behaved at lower temperatures, with a large range of predictable gel times. Colloidal silica gels may therefore have broad application to lower-temperature ($T \leq 200$ °C) geothermal systems and regions of lower temperature within hotter systems.

INTRODUCTION

In enhanced geothermal systems (EGS) the reservoir permeability is often enhanced or created using hydraulic fracturing. In hydraulic fracturing, high

fluid pressures are applied to confined zones in the subsurface usually using packers to fracture the host rock. This enhances rock permeability and therefore conductive heat transfer to the circulating geothermal fluid (e.g. water or supercritical carbon dioxide). The ultimate goal is to increase or improve the thermal energy production from the subsurface by either optimal designs of injection and production wells or by altering the fracture permeability to create different zones of circulation that can be exploited in geothermal heat extraction. Moreover, hydraulic fracturing can lead to the creation of undesirable short-circuits or fast flow-paths between the injection and extraction wells leading to a short thermal residence time, low heat recovery, and thus a short-life of the EGS.

A potential remedy to these problems is to deploy a cementing (blocking, diverting) agent to minimize short-cuts and/or create new circulation cells for heat extraction. A potential diverting agent is the colloidal silica by-product that can be co-produced from geothermal fluids. Silica gels are abundant in various surface and subsurface applications, yet they have not been evaluated for EGS applications. In this study we are investigating the benefits of silica gel deployment on thermal response of an EGS, either by blocking short-circuiting undesirable pathways as a result of diverting the geofluid to other fractures; or creating, within fractures, new circulation cells for harvesting heat through newly active surface area contact. A significant advantage of colloidal silica is that it can be co-produced from geothermal fluids using an inexpensive membrane-based separation technology that was developed previously (Bourcier et al., 2008).

This co-produced silica has properties that potentially make it useful as a fluid diversion agent for subsurface applications. Colloidal silica solutions exist as low-viscosity fluids during their “induction

period” but then undergo a rapid increase in viscosity (gelation) to form a solid gel. The length of the induction period can be manipulated by varying the properties of the solution, such as silica concentration and colloid size. We believe it is possible to produce colloidal silica solutions suitable for use as diverting agents for blocking undesirable fast-paths which result in short-circuiting the EGS once hydraulic fracturing has been deployed. In addition, the gels could be used in conventional geothermal fields to increase overall energy recovery by modifying flow.

We believe there may be additional advantages for using colloidal silica as blocking agents. It can be inexpensively produced on site or at other geothermal sites (Figure 1); it is inorganic and environmentally friendly as opposed to organic gels often used in oil/gas industry, and unlike conventional blocking agents, the gel material might be hydraulically removed after emplacement if needed. Furthermore, colloidal silica gelation can be triggered externally, for example by mixing with salt solutions or changing the pH, there should be fewer environmental restrictions and permitting requirements for its use given that the material originates in the same place it is to be injected, and silica removal in itself benefits the power plant in terms of silica scale control.

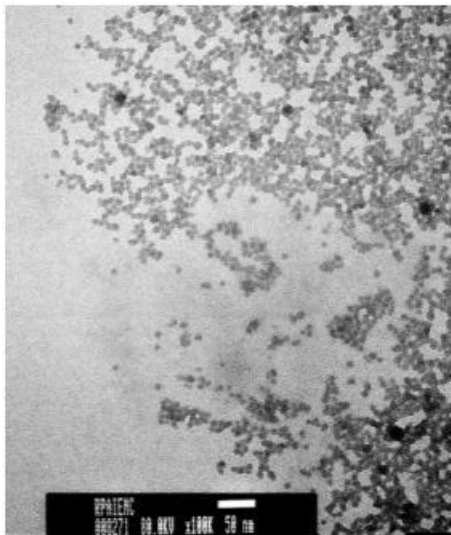


Figure 1: Silica gel produced from the Mammoth Lakes geothermal fluid. The gel is made up of a network of 10nm silica colloids (Bourcier, 2008).

To accurately predict when an injected geothermal fluid will set up and turn to gel, a quantitative understanding of the kinetics of silica gelation is required. Although silica gelation has been studied for decades, even the most comprehensive resources

(Iler, 1979; Bergna and Roberts, 2006) provide only a qualitative understanding of the various factors (pH, salt concentration, temperature, colloid diameter, SiO₂ concentration, etc.) that influence gelation times. Furthermore, much of the research on colloidal silica has been performed by the oil and gas and other industries (e.g., Jurinak and Summers, 1991; Vossoughi, 1999), and is therefore mostly proprietary. We did not find any quantitative method or model for predicting gel times from colloidal silica compositions. Such a method is needed to develop formulations for colloidal silica solutions for given geothermal applications. In addition, there is very little information on gel times at elevated temperatures. Because of these needs, we began an effort to acquire additional data that could be combined with the existing data to develop a more comprehensive quantitative model for use in our geothermal application.

METHODS

For our initial experiments at 25 °C, we used a Sunshine Instruments Gel Time Meter (Figure 2).



Figure 2: Sunshine Instruments Gel Time Meter (<http://www.davis.com>)

To use the Gel Time Meter, a sample is placed into a small polyethylene centrifuge tube which is in turn is set in a water bath. The temperature can be controlled within 1 °C. A stir rod is hung from a torsion wire and immersed into the sample, which will rotate when the power to the meter is turned on. Turning the power on also starts a time counter. The lower and upper electrical contacts are set 3/8” apart. The viscosity of the sample creates a drag on the rotation of the stir rod and the lower electrical contact, bringing the two contacts closer together. At a

certain threshold viscosity, the electrical contacts touch and the meter and counter shut off, recording the number of seconds between turning the meter on and reaching the threshold viscosity. This provides an accurate report of the gelation time of aqueous silica sols. The water bath can be used to bring the samples above ambient temperature, but because the stir rod must be lowered into the sample for the duration of the test, the water in the sample may escape due to evaporation or boiling.

The second instrument used in our experiments is a PVS rheometer from Brookfield Engineering, for experiments at elevated conditions (Figure 3). The PVS rheometer has an enclosed sample chamber, preventing sample boil-off. It can be operated up to ~200 °C and 1000 psi, and can provide an accurate, quantitative measure of sample viscosity as a function of time and/or shear rate, by measuring the torque exerted on an inner cylinder inside the sample chamber. The gel time meter provided only the time to gel formation and no viscosity vs. time data. The instrument enables measurement of both simple gelation times as well as non-Newtonian behavior, e.g., thixotropy, of colloidal silica sols and gels.



Figure 3: PVS Rheometer from Brookfield Engineering
(<http://www.brookfieldengineering.com>)

RESULTS AND DISCUSSION

25 °C Model (Gel Time Meter)

The gel time meter was used to quantitatively determine the effects of SiO₂ concentration, pH, and salt concentration on the gelation time of colloidal silica sols made with commercially available

LUDOX SM-30 at 25 °C, to provide a foundation for experiments at higher temperature. The major finding of this investigation is that there is a simple and clear relationship between gelation time and SiO₂ concentration. Previous investigations varied SiO₂ concentration while keeping pH and NaCl concentration constant. However, if the dilution is done by adding different amounts of water to identical mixtures of colloidal silica sol, NaCl, and HCl, a linear relationship arises between the logarithm of gelation time and the logarithm of the silica concentration (Figure 4). While the NaCl concentration and pH are changing as the mixtures become more diluted, the molar ratio of NaCl to SiO₂ and the molar ratio of added HCl to the Na⁺ stabilizer present in the colloidal sol (hereafter referred to as Cl⁻/Na⁺ ratio, which does not include either the chlorine or sodium from any added NaCl) remains constant.

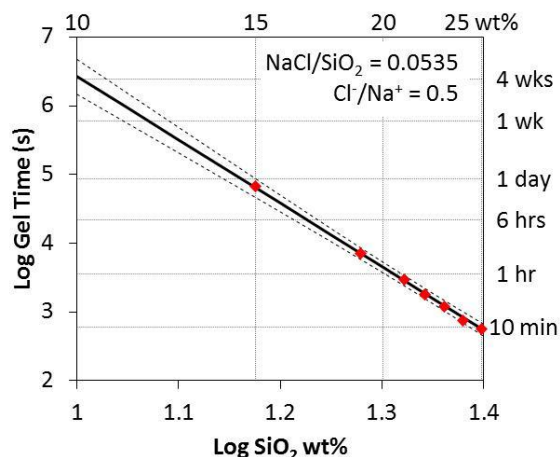


Figure 4: Log gel time vs. log silica concentration. Dashed lines are 95% confidence intervals over the entire model.

The relationship between gelation time and the molar NaCl/SiO₂ ratio (this ratio does not include any NaCl formed by the addition of HCl to the Na⁺ stabilizer) is more complex. Increasing the amount of salt while keeping all other variables constant initially has a large, decreasing effect on gelation time, but as more salt is added, the effect is diminished. However, adding salt will always decrease the gelation time. This has been modeled as a modified hyperbolic relationship (Figure 5).

The relationship between gelation time and Cl⁻/Na⁺ ratio is more complex still, as there are competing rate-limiting steps at low pH and high pH. Nevertheless, at near-neutral pH (6-9; Cl⁻/Na⁺ ratio = 0.5-1), the relationship can be modeled as a parabola (Figure 6).

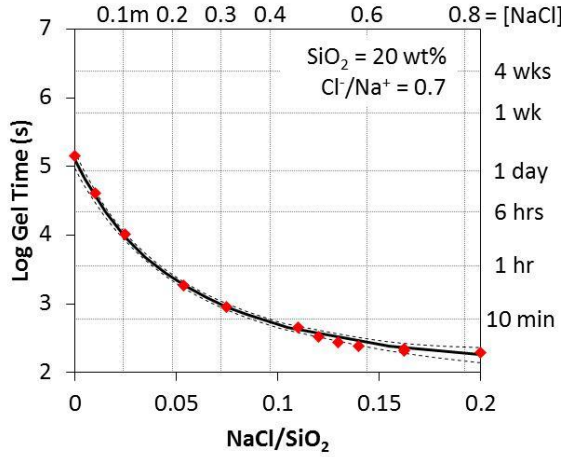


Figure 5: Log gel time vs. NaCl/silica ratio (NaCl created from the neutralization of Na^+ stabilizer with HCl is not included in this ratio). Dashed lines are 95% confidence intervals over the entire model.

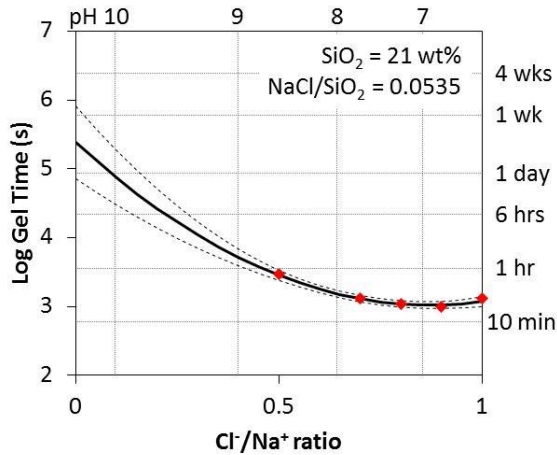


Figure 6: Log gel time vs. Cl^-/Na^+ ratio (added NaCl is not included in this ratio). Dashed lines are 95% confidence intervals over the entire model.

It should be noted that the top axes of Figures 5 and 6 depend upon the silica concentration, and are therefore not fixed relative to the bottom axes. Previous investigations of colloidal silica gels for the oil and gas industry have calibrated pH against Cl^-/Na^+ ratio (Jurinak, et al., 1991), but have neglected the effect of silica concentration on pH. We therefore performed our own calibration, based on

the most likely solutions that will be used in geothermal reservoirs. This calibration, in addition to the full model of gelation time, will be available on the geothermal data repository shortly.

The entire dataset (90 experiments) was fitted to a single equation with 11 regression parameters, as a function of SiO_2 wt%, molar NaCl/ SiO_2 ratio, and molar Cl^-/Na^+ ratio. The dashed lines in each of Figures 4-6 represent the 2σ errors for the entire regression. The regression equation ($R^2 = 0.9961$) is as follows:

$$\log(\text{Gel Time (s)}) = A \times \log(\text{SiO}_2 \text{ wt\%}) + B \quad (1)$$

where A and B are defined as follows:

$$A = \frac{\text{NaCl}}{\text{SiO}_2} \left(A_1 \left(\frac{\text{Cl}^-}{\text{Na}^+} \right)^2 + A_2 \left(\frac{\text{Cl}^-}{\text{Na}^+} \right) + A_3 \right) + A_4 \left(\frac{\text{Cl}^-}{\text{Na}^+} \right)^2 + A_5 \quad (2)$$

$$B = \left(\frac{\text{NaCl}}{\text{SiO}_2} + B_1 \right)^{-1} \left[B_2 \left(\frac{\text{Cl}^-}{\text{Na}^+} \right)^2 + B_3 \right] + B_4 \frac{\text{NaCl}}{\text{SiO}_2} + B_5 \left(\frac{\text{Cl}^-}{\text{Na}^+} \right) + B_6 \quad (3)$$

The numerical values of A_1 - A_5 and B_1 - B_6 are given in Table 1, and the error between prediction and measurement for each experiment is shown in Figure 7. No systematic error was observed over SiO_2 concentration, UN ratio, NaCl/ SiO_2 ratio, or observed gelation time. While most of the parameters were fitted by linear regression, it was not possible to fit parameter B_1 linearly. It was therefore fitted with non-linear regression (iterative use of Excel's solver and linear regression functions) to maximize the value of R^2 , and therefore does not have a well-defined error.

Table 1: Fitting Parameters for Equation 1.

Parameter	Value	Error (1σ)
A_1	-16.53	1.958
A_2	27.28	3.038
A_3	4.538	1.836
A_4	5.644	0.224
A_5	-11.37	0.220
B_1	0.067	N/A
B_2	-0.385	0.016
B_3	0.479	0.011
B_4	-18.16	1.761
B_5	-7.337	0.377
B_6	17.09	0.362

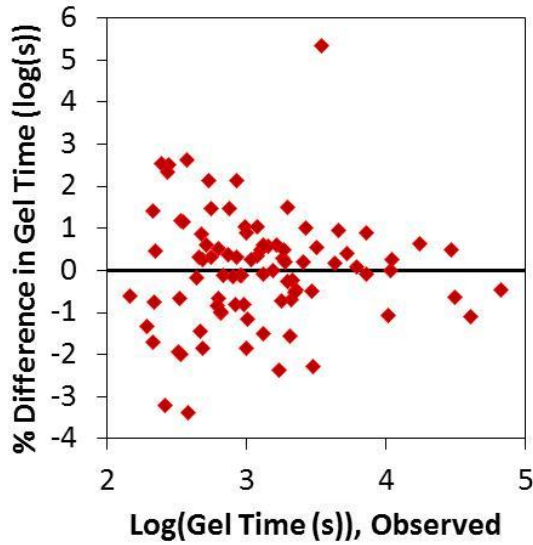


Figure 7: % Difference in Log(Gel Time (s)) between Predicted and Observed values vs. Observed Log(Gel Time).

High Temperature (PVS Rheometer)

Relationship between viscosity and gel time

Results from the rheometer indicate that gelation times can be reliably obtained from plots of viscosity over time, and that shear rate does not affect gelation time. An example of a viscosity over time plot is shown on Figure 8.

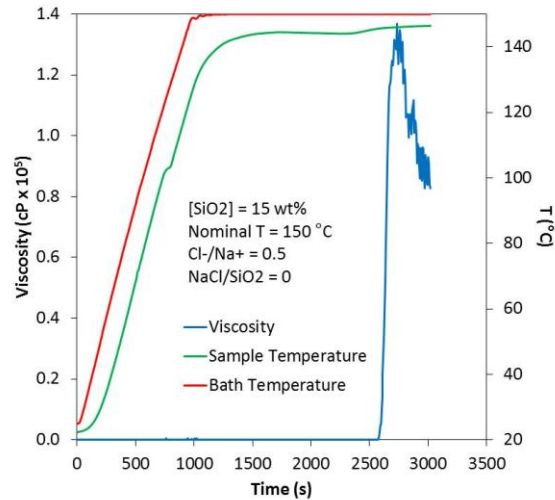


Figure 8: Viscosity (cP $\times 10^5$) as a function of time (seconds), measured at room temperature at a constant shear rate of 1 s^{-1} .

The data in Figure 8 are for a colloidal silica solution with 15 wt% SiO₂, a NaCl/SiO₂ ratio of 0 (no added

NaCl), and a Cl⁻/Na⁺ ratio of 0.5, subjected to a continuous shear rate of 1 s^{-1} and a nominal bath temperature of 150 °C. The viscosity remained near that for water for approximately 2600 seconds. During the gelation process, the colloidal solution starts thickening, the viscosity increases significantly, and reaches a maximum of 130000 cP at around 2700 seconds. After this point, the gel starts to slip past the inner cylinder rather than exerting a constant torque on it, causing the measured viscosity to drop and become irregular. However, the gel itself continues to stiffen and become brittle. Therefore, the information gathered after the maximum viscosity reached is irrelevant to this investigation.

Several experiments were repeated using different shear rates. The measured gelation time for each shear rate at 25 °C was within 2-3 minutes of the measured gelation time in the gel time meter; however, the maximum viscosity was dependent on the shear rate. If the shear rate doubles, the maximum viscosity recorded will be halved. This is entirely due to the interfacial layer of gel/water at the inner cylinder, and not reflective of the actual viscosity of the bulk gel as a whole. Therefore, at least in this experiment geometry, shear rate is not a significant variable when determining the gelation time.

Kinetics of silica gelation at elevated temperatures

We have investigated the effect of temperature on gelation time using the rheometer. Silica gels follow an Arrhenius relationship with temperature, shown in Equation 4, below.

$$\ln \left[\frac{t_{gel}(T)}{t_{gel}(T_0)} \right] = \frac{E_A}{R} \left[\frac{1}{T} - \frac{1}{T_0} \right] \quad (4)$$

However, in order to investigate kinetics experiments at elevated temperature, a finite sample heating time must be taken into account. In Figure 8, the sample temperature took approximately 15 minutes to approach the nominal temperature of the experiment, and gelled within 45 minutes of the start of the experiment. To say that the solution chemistry of Figure 8 gels in 45 minutes at 150 °C would therefore be inaccurate, as the sample did not reach its ultimate temperature for a full third of the duration of the experiment. Nor can we assume that because a finite heating time is always necessary, it can be cancelled out or ignored, as the heating path of the sample may not be the same in the laboratory and the field. However, this is not a problem for laboratory experiments, as a finite heating time for the sample can be taken into account as long as the temperature of the solution is known at all times. The nominal temperature of the experiment is therefore less

important than knowing the temperature vs. time history of the solution/gel.

For any given experimental heating path, we are missing several parameters from Equation 4. While the gel time of the experiment is measured, and the gel time of the chemistry at 25 °C can be modeled via Equations 1-3, we do not know the activation energy, nor do we have a single temperature to insert into the equation. To truly account for a finite heating time, Equation 4 must be integrated over time, with temperature being a function of time. This is shown in Equation 5, below.

$$t_{gel}(T_0) = \int_0^{t_{gel}} e^{\frac{-E_A}{R} \left(\frac{1}{T(t)} - \frac{1}{T_0} \right)} dt \quad (5)$$

Unfortunately, even if the experimental temperature as a function of time could be described by a functional form, this is an integral with no closed form solution, and must therefore be numerically calculated. For a given heating path, such as the one in Figure 8 above, $t_{gel}(T_0)$ can be numerically calculated using Equation 5 for a given value of E_A . The activation energy can therefore be solved for by using the modeled 25 °C gel time and a simple iterative solver, such as Excel's goal seek or solver functions. Once the activation energy is known for the particular experiment, a single "effective temperature" can be calculated using Equation 4. While it would be more accurate to measure the gel time of the same chemistry for multiple different heating paths (i.e., most likely to different nominal temperatures), set their integrals equal to each other to minimize the error in the activation energy and thereby avoid the use of extrapolated model values, this was not generally possible due to time constraints. However, this was performed on one solution chemistry, as a proof of concept and proof of the 25 °C model, shown below in Figure 9.

This solution chemistry (17 wt% SiO₂, Cl⁻/Na⁺ = 0.3) was run in two separate experiments. In the first, represented by path 1 in Figure 9, the sample was placed in the bath, and the bath was then set to a nominal temperature of 150 °C. This is roughly the same temperature path shown in Figure 8. The gel time using this temperature path was approximately 1 hour and 40 minutes. In the second experiment, represented by path 2 in Figure 9, the sample was held at 70 °C for approximately 10 hours, and then allowed to increase in temperature incrementally until the bath reached a temperature of 150 °C. The total gel time of this temperature path was approximately 17 hours.

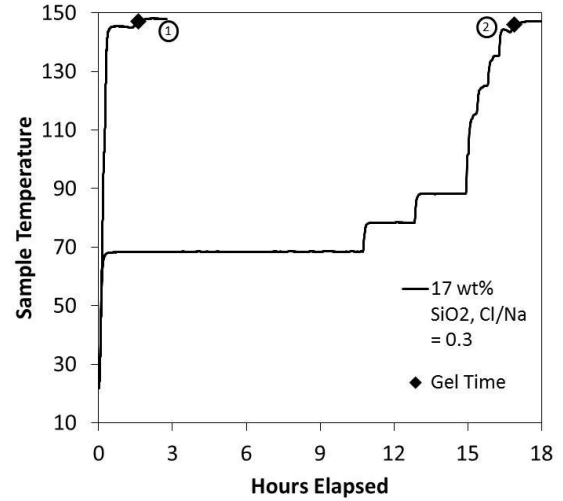


Figure 9: Gel time as a function of heating path.

This is of course not a substitute for a solution chemistry that will remain near 150 °C for 17 hours before gelling, but it does tell us two important things. First, that silica solutions can be held at lower temperatures (e.g. during injection into a geothermal well) for long periods of time without gelling, before being subjected to the temperature of the actual formation.

Second, these paths provide a check on the 25 °C model. Using Equations 1-5, the activation energy of the experiment following path 1 is 21.3 kcal/mol, and the activation energy of the experiment following path 2 is 21.8 kcal/mol. It is difficult to account for the experimental error involved in these paths, as changing the observed gel time involves changing the number of steps in the numerical integration, but given the calculated activation energies, an experimental error (in log units) of only 1.5% is needed to explain this discrepancy.

It should be noted that these reported activation energies are not true activation energies for a specific chemical mechanism of colloids networking together to create a gel. Colloid size plays an important role in the development of gels, and as a colloidal sol is heated, the equilibrium colloid size increases (Iler, 1979). As colloid size increases, there are fewer colloidal particles per unit volume, which actually should increase the gelation time. It is impossible to separate out these effects from each other unless the colloids are already larger than their high-T equilibrium size when they begin to heat. This is complicated even further when a complex temperature-time path is investigated, e.g. path 2 in Figure 9, as the colloids will have more time to come to their equilibrium size at an intermediate temperature. The most useful number, in this case, is

the observed activation energy of the overall process, which is reported here and can be used to predict gelation times given a starting chemistry and temperature-time path.

There is no observed effect of pressure on the gelation time, based on the fact that measurements conducted below 100 °C, without additional pressure, and measurements above 100 °C with 600 psi of N₂ gas pressure to keep the sample from boiling fell on the same Arrhenius line within error. Pressure may have an effect if the density of water deviates significantly from 1 g/cc, but this is unlikely to occur in geothermal reservoirs short of boiling, which, based on early tests above 100 °C without additional pressure, will significantly affect gelation. If the water boils, the concentration of silica in the remaining water will increase significantly, and will promote immediate local gelation and/or scale deposition at the water-steam interface.

Thermostability and avoiding precipitation

The work in the PVS rheometer has been limited to approximately 150-200 °C. It is certainly possible, however, to create colloidal silica gels at higher temperatures – Figure 10 shows a 15 wt% SiO₂ gel that was produced in a 300 °C oven, in a Swagelok capsule to keep water from escaping. These oven and capsule tests must be manually checked for the formation of a gel, so gel times cannot be precisely measured, but can be bracketed.



Figure 10: Gel (right) produced in a 300 °C oven. Water was prevented from escaping by sealing the colloidal solution in a Swagelok capsule (left). The shape of the gel reflects the internal geometry of the capsule.

The nominal temperature of the experiment was 300 °C, but it is unclear what the temperature vs. time history of the gelation process was. It is doubtful that the actual temperature of gelation was 300 °C,

because this process was completed within ten minutes.

After twenty minutes in a 300 °C oven, the gel still retained its solidity, but had turned white. In a gel, the silica network forms without changing local density: in other words, the silica particles do not aggregate and separate themselves from the water. A white “gel” indicates that the silica is in the process of aggregating, so that light can scatter off the regions of higher and lower density. After four hours, the gel had completely decomposed into a milky fluid, and over the next several days, the silica particles grew, separated from the water and settled down to the bottom of the capsule. This process is shown in Figure 11.

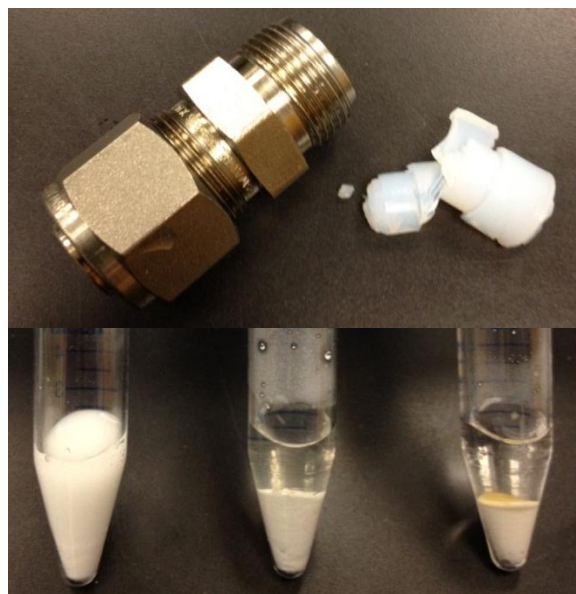


Figure 11: Above: Gel after 20 minutes at 300 °C. Below: Gel after 4 hours (left), 18 hours (center), and 72 hours (right).

This experiment was carried out at 200 °C as well, where the gel was stable for between 1 and 2 weeks. This large dependence on temperature implies that gels will be stable for months to years at even lower temperatures. The observed thermal stability does not appear to be dependent on silica concentration, as gels with 10 and 20 wt% SiO₂ also decomposed within several hours at 300 °C. It is therefore unlikely that colloidal silica gels will remain intact at such high temperatures for long periods of time. We therefore recommend that silica gels be used in low to medium temperature (<200 °C) geothermal reservoirs, though the amorphous silica created via decomposition of silica gel may also reduce fracture permeability. In that case the gel time serves to emplace the silica at the desired location. Later

decomposition to crystalline silica would maintain the reduced fracture permeability as desired.

One issue that arose in the course of our investigation at high temperature was that in some cases the silica precipitated on the walls of the sample chamber at the air/water interface as scale, instead of forming a continuous gel. While silica scale deposition at the interface was determined not to preclude the gelation of the bulk solution at a later time, a transition between regions of gelation to non-gelation does exist. Figure 12 shows a standard linear trend of gel time as a function of silica concentration. At 15 and 15.5 wt% SiO_2 , a typical brittle gel forms. At 14.5 wt% SiO_2 , though a well-defined gelation time exists, a ductile paste is formed instead of a brittle gel, denoted by the red outline on the data point. This ductile paste is shown in a weighing boat in Figure 13. A metal spatula is shown making an indentation into the paste, demonstrating its ductility. At 14 wt% SiO_2 , however, no gelation occurs. According to the linear trend of the other data points based on our overall model, a 14 wt% SiO_2 solution should gel or turn to paste in about 7-8 hours. We left this solution at a nominal temperature of 150 °C for 64 hours (denoted by the open square data point), and no gelation was observed. It is certainly possible that the solution will gel, turn to a ductile paste, or deposit all the silica as an amorphous solid on a longer time frame, but regardless, these solutions do not follow the linear trends that allow prediction of well-defined gelation times.

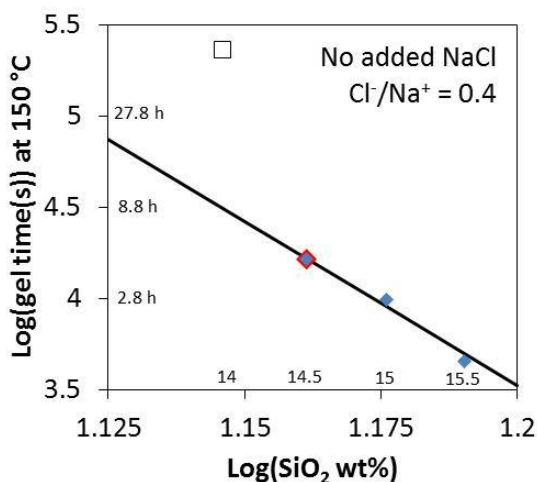


Figure 12: $\text{Log}(\text{gel time})$ vs. $\text{Log}[\text{SiO}_2]$ at 150 °C.



Figure 13: Ductile paste formed from a solution in the transition between gelation and non-gelation regimes.

Extension of gelation times at high temperature

Our investigation to extend gelation times at high temperatures while simultaneously ensuring that gelation actually occurs led us to vary both $[\text{SiO}_2]$ and the Cl^-/Na^+ ratio. Figure 14 shows the results of our investigation in this parameter space. While all of the experiments in Figure 14 were performed at a nominal temperature of 150 °C, they were not all at the same effective temperature (per analysis via Equations 4 and 5), due to the high variability in the ratio of heating time to the experiment duration. We have therefore modeled the activation energies of these solutions, and plotted the projected gel time at exactly 150 °C.

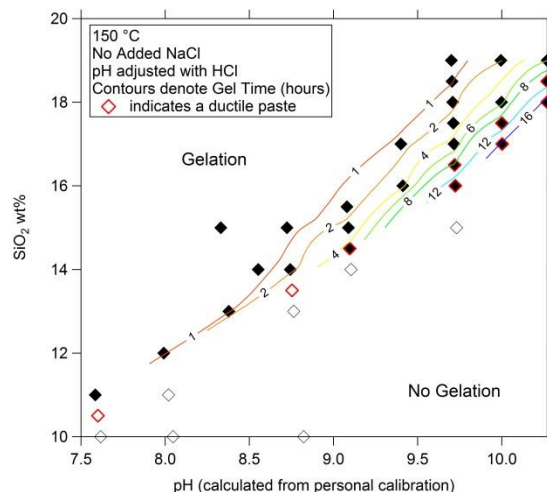


Figure 14: Contour plot of modeled gel times at 150 °C as a function of silica concentration and pH

The modeled activation energies were obtained by using Equations 1-5 to calculate the individual

experiments' effective temperature and activation energy. A linear regression was then performed on the activation energies as a function of silica concentration and Cl^-/Na^+ ratio. Activation energies were not modeled as a function of salt content. Due to the large effect that even a small amount of salt has on gelation time, we found that solutions containing any salt would gel too quickly for use at temperatures approaching 150 °C. The linear regression equation ($R^2 = 0.9608$) to calculate the activation energy in kcal/mol is as follows:

$$E_A = 16.18 \left(\frac{\text{Cl}^-}{\text{Na}^+} \right)^2 + \log([\text{SiO}_2]) \times \left(38.50 - 9.326 \left(\frac{\text{Cl}^-}{\text{Na}^+} \right) \right) - 24.41 \quad (6)$$

The open data points in Figure 14 denote experiments that did not gel, and the red outlined data points indicate solutions that turned into a ductile paste. Some of these pastes did not have a well-defined "gelation" time, and are open symbols. The longest gel time that produced a brittle gel at 150 °C in this investigation is 6 hours (19 wt% SiO_2 , $\text{Cl}^-/\text{Na}^+ = 0$), but pastes can be produced with "gelation" times of up to 17 hours (18 wt% SiO_2 , $\text{Cl}^-/\text{Na}^+ = 0$).

We also explored two other avenues of investigation: additives and colloid size. Sodium tetrafluoroborate (NaBF_4) has been successfully used in the oil industry to delay the onset of gelation for up to 12 hours at 100-120 °C (Jurinak, et al., 1991). At high temperatures, NaBF_4 slowly decomposes in water and forms HBF_4 and B(OH)_3 . Since both of these compounds are acids, this lowers the pH of the solution, which causes gelation. In effect, this would move a solution from the right to the left of Figure 14, from the non-gelation regime into the gelation regime, on a timescale determined by the decomposition of NaBF_4 . Unfortunately, it was found in the course of our investigation that the decomposition of NaBF_4 also depends on temperature, and while it can delay gelation up to 12 hours at 100-120 °C, the decomposition is much faster at 150 °C, and therefore does not provide an appreciable delay in gelation times at geothermal reservoir temperatures. Exploring other additives in more detail may be of use in future investigations.

The other parameter investigated is colloid size. While it was found that the 7-10 nm size of silica colloids produced from geothermal waters was relatively insensitive to on-site processing conditions (Bourcier, 2008), increasing the colloid diameter to larger values is commonly done in the silica manufacturing industry (Glen Mankin, Akzo Nobel, pers. comm.). Data for Ludox solutions show that

increasing the colloid size from 7 to 21 nm increases the gelation time by a factor of 40 at 25 °C at a constant silica concentration. However, gels created using large colloids are generally not translucent, indicating density heterogeneity. At high temperature, we found that these solutions deposited nearly all the silica present in solution as scale. While the scale was voluminous enough to be space-filling, it was very difficult to remove it from the sample chamber walls, needing several days in a 50 °C bath of concentrated NaOH. In the interest of time, we left a comprehensive investigation of large colloid size to future investigations.

As of the present moment, we can create gels at temperatures up to 150 °C easily, with brittle gel times as long as 6 hours (which will be lengthened in any real-world application, of course, due to the finite heating time required). From the activation energies determined in the course of this investigation, this indicates that gels at 175-200 °C can be created in as long as 1.2 hours and 17 minutes, respectively. By the same analysis, at lower temperatures (100-130 °C), a much larger range of gel times (up to days) can be achieved.

CONCLUSIONS

We have made significant progress in the determination of a new candidate agent for blocking, diverting, or modifying fracture flow networks in EGS systems. Results at high temperature indicate that it will be possible to choose formulations that will gel in a reasonable and predictable amount of time at the temperatures of EGS systems. Results from this study are informing concurrent work on modeling fluid flow in rough fractures. The modeling work, described in more detail by Bourcier et al. (this workshop), is proof-of-concept work of the positive impact of silica gel deployment. Gel deployments have previously been shown to enhance heat production in a single fracture (Ezzedine et al., 2012). LLNL's modeling effort this year has shown that gel deployments can also be tailored to minimize water losses from a circulation cell and block fast pathways in three-dimensional fracture networks in addition to the enhancement of heat production. We have also investigated gel deployments in sedimentary geothermal reservoirs.

Together, the experimental and modeling work will ultimately help increase the thermal energy production from EGS systems by altering the fracture permeability to create different zones of circulation that can be exploited in geothermal heat extraction.

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